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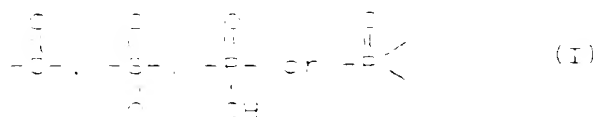
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(54) Title: ANTI-FOULING COATING COMPOSITIONS



(57) Abstract

An antifouling coating composition contains a biodegradable matrix, inorganic and organic, as hereinafter described, containing at least one solid inorganic material at least one terminal anion of the formula $-\text{X}-\text{O}-\text{M}-\text{P}-$, wherein X represents Cl, M represents a metal having a valency of at least 2, X represents 1 or 2, and R represents a monohydroxy, dihydroxy and trihydroxy. The coating composition contains a substantially non-volatile amine which reacts with the hydroxy groups of the matrix to form a cross-linked polymer.

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ANTIFOULING COATING COMPOSITIONSTechnical Field

This invention is concerned with antifouling coating compositions used on surfaces likely to come into contact with marine fouling organisms such as algae, seaweed and barnacles, for example on ships or boats or on the outfalls for cooling water from power stations. Such coating compositions generally comprise a biocide for marine organisms and a binder polymer.

10 Background Art

There have been many suggestions in recent years for self-polishing antifouling paints having binders which are linear polymers containing pendant side groups which are liberated from the polymer by reaction with seawater, the residual polymer being sufficiently dispersible or soluble in seawater to be swept away from the paint surface, exposing a fresh layer of the binder able to undergo a similar reaction with seawater. Such paints are described for example in GB-A-1457590. The gradual thinning of the paint film controls the release of a biocide active against fouling. The only commercially significant self-polishing paints employ binders which comprise triorganotin ester leaving groups.

EP-A-204456 describes a hydrolysable resin for use in antifouling coatings consisting of a resin having at least one side chain bearing at least one terminal group of the formula:

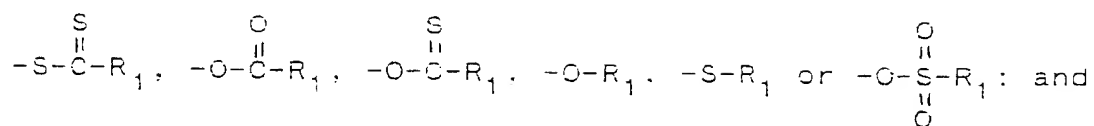


30 where n represents $\begin{matrix} 1 & 2 & 3 \\ | & | & | \\ -O- & -O- & -O- \end{matrix}$ or $-R$ $\begin{matrix} 1 & 2 & 3 \\ | & | & | \\ -O- & -O- & -O- \end{matrix}$

M is a metal selected from zinc, cadmium and tellurium;

x is an integer of 1 to 2; R represents an organic group.

residue selected from:



- 5 R_1 is a monovalent organic residue.

EP-A-342276 describes a process for preparing such a metal-containing resin composition comprising reacting a mixture of:

- (A) an acid group-containing resin;
 10 (B) a metallic salt of a low-boiling organic acid, in which the metal is selected from those having 2 or more valences and a lesser ionization tendency than those of alkali metals; and
 (C) a high-boiling organic monobasic acid;
 15 at an elevated temperature while removing the formed low-boiling organic basic acid out of the system.

- US-A-2490925 discloses a pest-control composition comprising stabilised rosin amine or a co-ordinate covalent metal salt thereof dispersed in kerosine, gasoline, ben-
 20 zene, alcohol, acetone, water or pine oil. The composition is stated to be particularly effective as a fungicide. The composition can be added to marine paint containing a dehydroabietylamine complex of copper acetate.

- JP-A-54-64633 describes a marine antifouling biocide
 25 which is a long-chain (12 to 18 carbon atoms) linear aliphatic primary amine or salt thereof. JP-A-54-110322 describes certain long-chain (12 to 18 carbon atoms) linear aliphatic secondary and tertiary amines as marine antifoul-
 ing agents.

- 30 US-A-4675051 describes a marine antifouling paint which is gradually dissolved in seawater and which comprises a binder which is a resin produced by the reaction of rosin and an aliphatic polyamine containing at least one

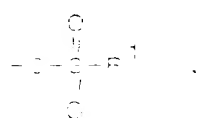
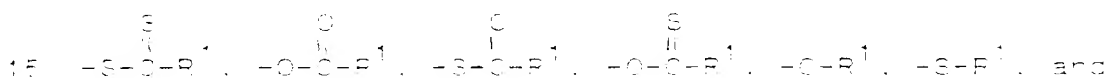
carboxylic-acid-functional polymer of equivalent weight 240 to 600. A preferred acid-functional polymer is an addition copolymer of one or more olefinically unsaturated acids or anhydrides, for example acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid or itaconic anhydride, vinyl benzoic acid (for example p-vinyl benzoic acid), 3-butenoic acid or beta-carboxy-ethyl acrylate or methacrylate, with at least one olefinically unsaturated comonomer. Copolymers of methacrylic acid or acrylic acid are preferred. (The preferred equivalent weight of 240 to 600 corresponds to an acrylic acid content of 14.3 to 35.8% by weight and a methacrylic acid content of 16.7 to 41.7% by weight). The acid monomer is preferably copolymerised with one or more comonomers which are unreactive with acid groups, for example acrylic or methacrylic esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate or 2-ethylhexyl methacrylate, styrene, acrylonitrile, vinyl acetate, vinyl butyrate, vinyl chloride, or vinyl pyridine. Terpolymers may be preferred, for example methyl methacrylate or ethyl methacrylate, which tend to form a hard film, can be used in conjunction with an acrylate such as ethyl acrylate or particularly an alkyl acrylate of 3 to 8 carbon atoms in the alkyl moiety such as butyl acrylate, which helps to form a more flexible film. Such an acid polymer preferably has a molecular weight of 1,000 to 100,000. The equivalent weight of the acid polymer (calculated as acid groups) is most preferably 300 to 440, equivalent to an acrylic acid or methacrylic acid content of about 20 to 30% by weight.

Alternative carboxylic acid-functional polymers are alkyd resins.

Alternative acid-functional polymers are polymers containing sulphonic acid, phosphonic acid or phosphoric acid (acid phosphate) groups. If alternative acid groups are used they are also preferably present in an addition polymer, for example an addition copolymer of an olefini-

allyl, unsaturated proacetic, phosphonic or sulfonic acid. Examples of such unsaturated acids are vinyl proacetic acid, styrene proacetic acid, 2-acrylamidopropane proacetic acid, ethylidene-1, 1-diphosphonic acid, hydroxy-5 ethyl acrylate monophosphate, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid, methallyl sulfonic acid and styrene sulfonic acid. Polymers containing stronger acid groups such as sulfonic acid groups may have a higher equivalent weight, for example in 10 the range 500 to 5000, preferably 1000 to 2000.

The monobasic organic acid residue R which is incorporated in the hydrolysable resin is preferably selected from:



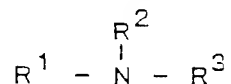
wherein R¹ represents a monovalent organic residue linked 20 through a carbon atom. The group R¹ can alternatively represent an amino group.

When the process of EP-A-342278 is used, the metallic salt which is reacted with the base resin and the high-boiling acid is a salt of the metal M and a low-boiling organic acid such as acetic acid or propanoic acid. The 25 high-boiling acid RH, whose residue R is incorporated in the hydrolysable resin, preferably has a boiling point at least 20°C higher than that of the low-boiling organic acid. The high-boiling acid RH can be a carboxylic, sulfonic, thiocarboxylic, thiosulfonic, carbamic, thiocarbamic, thiothiocarbamic, dithiocarbamic or dithiothiocarbamic acid. The acid RH is preferably a carboxylic acid, most preferably an aliphatic carboxylic acid having

at least 8, for example 12 to 20, carbon atoms, for example lauric, stearic, oleic, linoleic, ricinoleic or 12-hydroxystearic acid; alternative carboxylic acids include benzoic, salicylic, nitrobenzoic, chloroacetic, dichloro-
 5 acetic or chlorobenzoic acid. The acid can be a mixture of carboxylic acids such as the mixed aliphatic carboxylic acids sold as naphthenic acid or versatic acid, or a mixture of acids derived from a natural fat or oil. Alternative acids include toluenesulphonic, beta-naphthalenesulphonic, p-chlorobenzenesulphonic, dimethyldithio-
 10 carbamic and diethyldithiocarbamic acid.

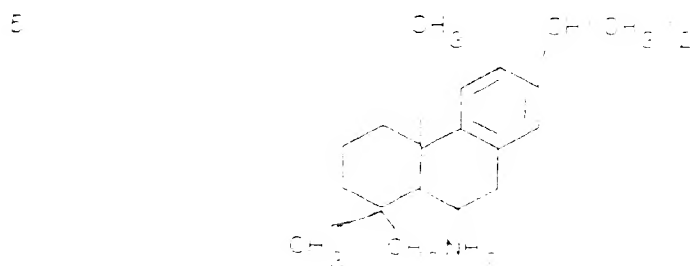
The base resin, metallic salt and high-boiling acid are generally reacted at a temperature above the boiling point of the low-boiling acid but below the boiling point
 15 of the high-boiling acid to form the hydrolysable resin. The reaction is preferably carried out in an organic solvent, for example a hydrocarbon such as xylene or trimethylbenzene, a ketone such as methyl isoamyl ketone or an ester such as butyl acetate, ethoxyethyl acetate or
 20 methoxypropyl acetate.

The amine used in the coating composition is substantially non-volatile at ambient temperature (20°C) and standard pressure. Preferably, it has a boiling point of at least 200°C, most preferably at least 250°C. The amine
 25 is preferably a monoamine and is preferably a primary amine, although a secondary or tertiary amine can be used. The amine preferably includes at least one organic group containing at least 10 carbon atoms, more preferably 12 to 20 carbon atoms. Such amines generally have the advantage
 30 that they are toxic to marine organisms. The amine can for example be a diterpene-derived amine of the formula:



where R¹ is a monovalent hydrocarbon group derived from a
 35 diterpene and R² and R³ are each independently hydrogen, an alkyl group having 1 to 18 carbon atoms or an aryl group

having 8 to 12 carbon atoms. Such an amine is preferably derived from rosin. A primary amine derived from rosin is den. broabnety amine (as a commercial), as Rosin Amine D. Its main constituent is:



A corresponding secondary or tertiary amine, for example an N-methyl or N,N-dimethyl derivative of Rosin Amine D, can alternatively be used. The diterpene amines are effective marine biocides. The amine can alternatively be an aliphatic amine containing an organic group of 12 to 20 carbon atoms, for example a straight-chain alkyl or a kenyl primary amine such as dodecyl amine, hexadecyl amine, dotadecyl amine or oleyl amine or mixtures of amines derived from aliphatic groups present in natural fats and oils such as tallow amine or hydrogenated tallow amine or coconut amine (coco-amine) or a corresponding secondary amine or tertiary amine such as N-methyl dodecyl amine or N,N-dimethyl coco-amine. The long chain aliphatic amines having 12 to 16 carbon atoms are very effective marine biocides. Alternative amines which can be used are aralkylamines such as those sold commercially as "phenylamines", or hydroxy-substituted amines such as tri-ethanolamine or diethanolamine.

The anti-fouling coating composition is preferably applied as a solution in an organic solvent, for example a hydrocarbon such as xylene or white spirit, a ketone such as methyl isobutyl ketone or methyl isobutyl ketone, or an alcohol such as methanol, ethoxyethanol or methoxypropane or an ester such as butyl acetate, ethoxy-ethyl acetate or methoxyethyl acetate. When the mixture

lysable resin binder is prepared in an organic solvent the resin solution can be used directly in preparing the paint. It can optionally be diluted by further solvent, preferably selected from the solvents listed above.

5 The non-volatile amine has the advantage that it reduces the viscosity of solutions of the hydrolysable resin in organic solvents such as those listed above. The amine is believed to react at least in part to form a co-ordination complex with the metal M in the hydrolysable
10 resin. In the co-ordination complex the metal M may be co-ordinately bonded both to the amine as ligand and to an anion, for example a carboxylate anion, acting as organic acid residue R. For those metals which form coloured hydrolysable resin solutions complex formation can be seen
15 by a colour change. Solutions of hydrolysable resin in which the metal M is copper, for example, are generally green in the absence of amine but change colour to blue when the amine is added. The amine can reduce the viscosity of the hydrolysable resin solution by a factor of up
20 to 4. The amine can thus be used with hydrolysable resin solutions which without amine are too viscous to form the basis of a sprayable paint, that is hydrolysable resin solutions which have an increased resin content. For example, the amine can be added to hydrolysable resin
25 solutions having a resin content of 30 to 35 per cent by volume to produce solutions whose viscosity is equal to that of hydrolysable resin solutions without amine having a resin content of 25 to 30 per cent by volume. Moreover, since the amine is non-volatile it also directly increases
30 the non-volatile content of the coating composition. There has been recent pressure for the use of a reduced content of volatile organic solvent in various types of coating compositions.

35 The proportion of hydrolysable resin to amine in the coating composition is preferably from 98:2 to 10:90 by volume, most preferably from 90:10 to 30:70. Amines having

no film-forming properties are preferably used at no more than 40% based on the combined weight of polymer and amine, whereas film-forming amines such as the diterpene derivatives can be used at a higher proportion if desired. More than one amine can be used: for example a diterpene amine can be used with a long-chain aliphatic amine.

If an amine which is biocidal to marine organisms is used, the resulting coating composition comprising hydrolysable resin and amine can be used as a clear antifouling varnish or can be pigmented. If the metal M in the hydrolysable resin is a metal which is toxic to marine organisms, for example copper, it can augment the marine biocidal properties of the coating, although since the metal content of the hydrolysable resin is only for example 10 to 15% by weight its effect may not be large.

If a non-biocidal amine is used the coating composition should contain a marine biocide. The coating preferably contains a pigment, and the same material may function simultaneously as a marine biocide and as a pigment if a biocidal pigment is used.

The amine is preferably pre-mixed with the hydrolysable resin binder before addition of other components of the coating. The hydrolysable resin binder solution can alternatively be mixed simultaneously with the amine and with the pigment. For example, the hydrolysable resin solution and the amine can be mixed with pigment using conventional paint blending procedures to provide a composition having a pigment volume concentration of, for example, 25 to 55%. The pigment is preferably a sparingly soluble pigment having a solubility in seawater of from 0.5 to 100, most preferably 1 to 10, parts per million by weight, and is preferably a metaliferous pigment. The pigment is most preferably a copper or zinc compound, for example cuprous oxide, cuprous trihydroxide, zinc oxide, zinc dimethyl dithiocarbamate, zinc diethyl dithiocarbamate

bamate, cuprous ethylene bis(dithiocarbamate) and zinc ethylene bis(dithiocarbamate). These sparingly soluble pigments which are copper and zinc compounds are generally also marine biocides. The sparingly soluble metalliferous pigments produce water-soluble metal compounds on reaction with seawater so that the pigment particles do not survive at the paint surface. Mixtures of sparingly soluble pigments can be used, for example cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate), which are highly effective biocidal pigments, can be mixed with zinc oxide, which is less effective as a biocide but dissolves slightly more rapidly in seawater.

The paint composition can additionally or alternatively contain a pigment which is not reactive with seawater and may be highly insoluble in seawater (solubility below 0.5 part per million by weight) such as titanium dioxide or ferric oxide or an organic pigment such as a phthalocyanine pigment. Such highly insoluble pigments are preferably used at less than 40% by weight of the total pigment component of the paint, most preferably less than 20%.

The anti-fouling paint can also contain a non-metalliferous biocide for marine organisms, for example tetramethyl thiuram disulphide, methylene bis(thiocyanate), captan, a substituted isothiazolone, for example as described in GB-A-1575226, or 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine.

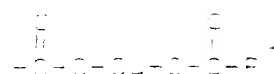
The invention is illustrated by the following Examples:

Examples 1 to 4

A 28.9% by volume solution A in a 4:1 xylene:butanol mixture of a hydrolysable resin based on a methacrylic acid copolymer with acrylate and methacrylate esters, in which the pendent carboxylic groups derived from the methacrylic

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acid has been converted to



groups, wherein R^1 is derived from a high boiling aliphatic carboxylic acid (naphthoic acid or similar), was
 5 mixed with Rosin Amine D in the proportions shown in Table 1 below. The ratio of mixing is quoted as a volume ratio of hydrolysable resin to Rosin Amine D on a dry weight basis. The green resin solution and colourless amine
 10 formed a blue solution, the blue colour being most intense at a mixing ratio of 40:60 (Example 3).

Table 1

Example No.	Mixing Ratio	Solids Content % by volume	Viscosity in mPa s
15 1 (A)	100:0	28.9	240
2	80:20	33.7	81
3	60:40	40.4	80
4	40:60	50.4	180
5	20:80	67.0	180

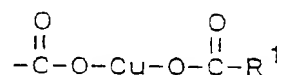
20 As shown in Table 1, the addition of Rosin Amine D decreased the viscosity of the hydrolysable resin solution (Rosin Amine D is itself a viscous liquid resin of viscosity well above 1000 mPa s). The products of Examples 1
 25 to 4 can be used as clear antifouling varnishes. Alternatively, they can be mixed with pigments, for example broadal pigments known for use in antifouling paints such as cuprous oxide, cuprous thiocyanate or zinc ethylene bis dithiocarbamate).

Examples 5 to 12

30 The process of Examples 1 to 4 was repeated using two

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different hydrolysable resin solutions, each being acrylic resins containing pendent groups of the form:



- 5 The viscosities after mixing are shown in Table 2. The hydrolysable resin solution B of Examples 5 to 8 had a solids content of 27.6% by volume and the solution C of Examples 9 to 12 a solids content of 29.5% by volume.

Table 2

10	Example No.	Mixing Ratio	Solids Content	Viscosity
			% by volume	in mPa s
	(B)	100:0	27.6	240
	5	80:20	32.3	100
	6	60:40	38.9	100
15	7	40:60	48.8	260
	8	20:80	65.6	290
	(C)	100:0	29.5	360
	9	80:20	34.3	110
	10	60:40	41.0	120
20	11	40:60	51.1	180
	12	20:80	67.6	280

Examples 13 to 21

- Hydrolysable resin solution (A, B or C above), pigment and Rosin Amine D were mixed by conventional paint mixing technology in a high-speed disperser to form paints of the compositions shown in Table 3 (amounts of ingredients in % by weight).

- The paints of Examples 13 to 21 were applied to primed steel panels and were immersed in seawater in an area rich in marine fouling. After 12 months' immersion they

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resisted fouling by algae and animal fouling, whereas a non-toxic comparison panel showed heavy fouling.

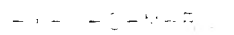
The paints of Examples 18, 20 and 21 were applied as test patches below the waterline on the side of the hull of an oil tanker. After 11 months in service, mainly at tropical latitudes, the test patches were substantially free from algal and animal fouling, whereas a neighbouring patch not coated with antifouling paint was heavily fouled.

Table 3

Example No.	13	14	15	16	17	18	19	20	21
Hydrolisable Resin Solution	21.52(A)	22.47(B)	22.99(C)	26.38(A)	24.23(B)	24.64(C)	33.13(A)	34.12(B)	32.83(C)
Rosin Amine D	5.03	7.00	6.46	5.14	6.29	5.77	6.64	6.54	6.67
Chlorinated paraffin plasticiser	3.48	4.07	4.07	3.95	4.01	4.02	-	-	-
Cuprous Oxide	46.55	54.48	54.49	52.89	53.66	53.75	54.05	53.25	54.29
Titanium Dioxide	2.87	3.35	3.35	3.26	3.30	3.31	-	-	-
Red Iron Oxide	-	-	-	-	-	-	4.16	4.10	4.18
Structuring Agents (bentonite, clay and silica)	1.74	2.04	2.04	1.98	2.01	2.01	2.02	2.00	2.03
Methyl isobutyl ketone	10.46	3.66	3.67	3.56	3.61	3.62	-	-	-
Xylene	8.36	2.93	2.93	2.85	2.89	2.89	-	-	-
Volume ratio of hydrolisable resin to amine	56:44	49:51	53:47	61:39	53:47	56:44	60:40	60:40	60:40
% solids content by volume	38.3	53.0	53.1	50.0	51.4	51.7	53.2	51.6	53.9
Paint viscosity (poise)	-	-	-	-	-	-	4.4	5.5	6.9

CLAIMS

1. An antifouling coating composition containing a
 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995



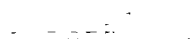
wherein R represents: $-\text{O}-$, $-\text{C}(=\text{O})-$, $-\text{C}(=\text{O})-\text{O}-$, or $-\text{C}(=\text{O})-\text{NH}-$.

10 W represents a metal having a valency of at least 2,
 5 R represents 1 or 2, and R represents a monophasic organic
 acid residue, characterised in that the coating composition
 contains a substantially non-volatile amine.

2. An antifouling coating composition according to
 15 claim 1, in which R represents $-\text{O}-$, characterised in that
 the hydrolysable resin is derived from a carboxylic acid-
 functional polymer of acid equivalent weight 240 to 600.

3. An antifouling coating composition according to
 20 claim 1 or claim 2, characterised in that the metal W is
 copper or zinc and x is 1.

4. An antifouling coating composition according to
 any of claims 1 to 3, characterised in that the monophasic
 organic acid residue R is selected from:



wherein R^1 represents a monovalent organic residue linked through a carbon atom.

5. An antifouling coating composition according to claim 4, characterised in that the monobasic organic acid residue R is the residue of an aliphatic carboxylic acid having at least 8 carbon atoms.

6. An antifouling coating composition according to any of claims 1 to 5, characterised in that the substantially non-volatile amine includes at least one organic group having at least 10 carbon atoms.

7. An antifouling coating composition according to claim 6, characterised in that the said organic group having at least 10 carbon atoms is derived from a diterpene.

8. An antifouling coating composition according to claim 6, characterised in that the substantially non-volatile amine is an aliphatic amine containing an organic group of 12 to 20 carbon atoms.

9. An antifouling coating composition according to any of claims 1 to 8, characterised in that the proportion of hydrolysable resin to amine in the coating composition is from 90:10 to 30:70 by volume.

10. An antifouling coating composition according to any of claims 1 to 9, characterised in that the amine is present at least partly as a ligand in a co-ordination complex with the metal M in the hydrolysable resin.

11. An antifouling coating composition according to any of claims 1 to 10, characterised in that it contains a pigment which is a copper or zinc compound having a solubility in seawater of from 0.5 to 100 parts per million by weight.

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12. A process for preparing an antiseal and coating composition containing a silicate filler, reactive organics and comprising as binder a hydrolyseable resin having at least one side chain bearing at least one terminal group of the formula:



wherein x represents $\begin{matrix} \text{O} & \text{O} & \text{O} & \text{O} \\ | & | & | & | \\ -Si- & -Si- & -Si- & -Si- \\ | & | & | & | \\ \text{O} & \text{O} & \text{O} & \text{O} \end{matrix}$ or $-P<$.

13. M represents a metal having a valency of at least 2, x represents 1 or 2, and R represents a monobasic organic acid residue, characterised in that a substantially non-volatile amine is incorporated into the composition.

14. A process according to claim 12, characterised in that the amine forms a co-ordination complex with the metal M in the hydrolyseable resin.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 91/00561

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 09 D 5/14		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 09 D	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁸		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A, 0342276 (NIPPON PAINT CO.) 23 November 1989 cited in the application	
A	EP, A, 0204456 (NIPPON PAINT CO.) 10 December 1986 cited in the application	

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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
7th June 1991	22 JUL 1991	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	MISS T. TAZELAAR	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 16-07-91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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